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(54) Triglycerides rich in polyunsaturated fatty acids

(57) Triglycerides, having at least two long chain polyunsaturated fatty acids L_1 and L_2 , from which at least one is present for more than 20 wt%, while the weight ratio $L_1:L_2$ is at least 2 and which triglycerides also contain at least 15 wt% of saturated fatty acids with 14 or more carbon atoms and have a weight ratio saturated C_{18} : saturated C_{16} fatty acid residue of > 2 , while at least 5 wt% of the saturated fatty acid residues with at least 14 C-atoms is bonded on a triglyceride molecule, wherein also L_1 and/or L_2 is present, display a number of beneficial properties (good oxidative stability healthier, less off-flavour, lower caloric, better digestibility, and in particular better structuring properties).

EP 0 739 591 A1

Description

According to EP 265 699 fats with a superior digestibility and absorptivity are obtained, when these fats are composed of triglycerides having a specific amount of C_8 to C_{14} fatty acid residues at the 2-position, while residues with C_{18} or higher fatty acids are bonded at the 1,3-positions. Typical examples of the C_{18} and higher fatty acids are polyunsaturated fatty acids, such as arachidonic acid, eicosapentenoic acid and docosahexenoic acid. However nothing is disclosed about fat compositions that combine in the fat saturated fatty acid residues and at least two different long chain polyunsaturated fatty acid residues and that have structuring properties.

In WO 90/04012 it is disclosed that triglycerides that contain saturated C_8/C_{10} fatty acid residues in 1,3 and simultaneously a polyunsaturated fatty acid residue (in particular DHA) in the 2-position, have beneficial nutritional properties, in particular for enteral or parenteral purposes. However again, nothing is disclosed about fat compositions that contain in the fat specific amounts of saturated and two different polyunsaturated fatty acid residues and that have structuring properties.

From WO 94/00044 it is known that fatblends that contain unhardened fish oil have significant health benefits. Fish oil often contains appreciable amounts of two different polyunsaturated fatty acids, e.g. DHA and EPA. However it is also known that fish oil has a number of draw backs. A particular disadvantage of fish oils being that they do not have structuring properties, which makes it difficult to apply them in fat compositions wherein a structuring agent is required in order to give the fat composition a performance, that is desired to make the fat applicable in foodproducts.

Toyoshima c.s. disclosed in Journ. of the Japan Oil chem Soc 42 (11), 1993, pages 30-35 a transesterification process, applying *Mucor miehei* as enzyme of a fish oil, such as sardine oil. EPA concentrated oil or DHA concentrated oil with polyunsaturated fatty acids. This resulted in triglycerides with about 62 % of PUFA in it. It is further disclosed that EPA was incorporated more easily than DHA. Therefore triglycerides high in DHA were made by an additional transesterification in the fish oil/PUFA system. This document therefore does not disclose triglycerides rich in a first LCPUFA and containing a second LCPUFA in a weight ratio of > 2 , which triglycerides further contain saturated C_{14} , fatty acids.

Endo in Bioscience Biotechn Biochem 57 (12) 1993, pages 2202-2204 discloses that sardine oil can be stabilized by interesterification with saturated or mono-unsaturated fatty acids. However, the effects with stearic acid are very low. As a result of the enzymic interesterification the total amount of LCPUFA in sardine oil (was 20 %) decreased to 17.5 wt % if stearic acid groups were introduced. Therefore, this document does not teach triglycerides rich in a first LCPUFA and also containing a second LCPUFA in a ratio of > 2 , while also at least 15 wt% C_{14} , saturated fatty acids were present in the triglycerides.

From US 5,151,291 can be concluded that triglycerides, rich in EPA with good properties to make them suitable for margarine applications can be obtained by a process wherein EPA-ester is converted with a "higher fatty acid" triglyceride. Higher fatty acid triglycerides are defined as saturated or unsaturated C_{14+} fatty acid triglyceride.

They include palmitic, stearic but also oleic, linoleic, EPA and DHA. However, this method will never result in triglycerides containing two different LCPUFA's in a ratio of > 2 , while simultaneously saturated C_{14+} fatty acid will be present. Moreover this document does not disclose the impact of the $C_{18,9}/C_{16,9}$ -ratio in the products on the structuring properties of the fats.

EP 271,909 discloses triglycerides, wherein simultaneously three different fatty acid residues are present. These residues are selected from $C_{20} \cdot C_{22}$ saturated or (poly)unsaturated fatty acids; $C_{14} \cdot C_{18}$ saturated or unsaturated fatty acids and $C_6 \cdot C_{12}$ saturated or unsaturated fatty acids. The products never comprise two different LCPUFA's in a ratio of > 2 in combination with > 15 wt % saturated C_{14+} fatty acid.

We have performed a study to find out, whether fat compositions existed, that could overcome the draw backs of the known fat compositions, while they would retain the beneficial effects of the presence of relatively high amounts of polyunsaturated fatty acids. This study has resulted in the finding of novel fats, that combine the following beneficial product properties:

- our novel fats display an oxidation stability which is not lower than for known triglycerides with similar compositions, but not having our levels of specific saturated fatty acids present;
- our novel fats are better for the development of the brain, in particular when consumed by infants. This effect is due to the relatively high levels of docosahexenoic acid (DHA) in our fats;
- our novel fats also can contain relatively high levels of eicosapentenoic acid (EPA), which makes our fats healthier, due to the effect of EPA on coronary diseases;
- our novel fats, containing C_{16}/C_{18} saturated fatty acids in our specific ratio's display better flavour characteristics than the fats containing C_{14} saturated fatty acids; this is due to the fact that C_{14} leads to a faster hydrolysis and thus to the development of a quicker off-taste than C_{16}/C_{18} ;

- our novel fats, containing relating high levels of C_{18} saturated fatty acid residues, display a lower caloric behaviour. This is due to the fact that C_{18} saturated fatty acid, displays a reduced fat absorption by the body and thus displays a decreased digestibility. This is also the reason why the fats, based on C_{18} saturated fatty acids are healthier than the fats based on C_{14} or C_{16} saturated fatty acids.

- our fats, based on C_{18} -saturated fatty acids will also be healthier due to cholesterol lowering effects over C_{14} and C_{16} acids;

- our novel fats with the specific $C_{18:0}/C_{16:0}$ display better structuring properties than fats with lower levels of $C_{18:0}$ and higher levels of $C_{16:0}$;

- our novel fats can be obtained as a result of interesterification reactions, in particular enzymic interesterification, which results in fats with a better triglyceride-distribution than known fats. Simultaneously these fats will display an improved melting behaviour as our fats will hardly contain any trisaturated triglycerides.

So our invention concerns with novel fats, that display one or more of above beneficial effects.

Our novel fats can be described as a triglyceride-composition, comprising at least two long chain polyunsaturated fatty acids L_1 and L_2 , both having at least 3 unsaturations and having at least 20 carbon atoms from which L_1 is the most abundant and L_2 is the second most abundant, wherein the triglyceride composition contains at least 20 wt% of L_1 , while the weight ratio $L_1:L_2$ is at least 2, and the triglyceride composition also contains at least 15 wt% of saturated fatty acids with 14 or more carbon atoms, and wherein the weight ratio $C_{18:0}:C_{16:0}$ is > 2 , whereas at least 5 wt%, preferably at least 10 wt%, most preferably at least 20 wt% of the saturated C_{14+} fatty acid residues is bonded on a triglyceride molecule, wherein at least L_1 and/or L_2 is present.

Preferred fats are triglyceride compositions according to claim 1, wherein the amount of L_1 is more than 30 wt%, while the weight ratio $L_1:L_2$ is at least 3, while triglyceride compositions according to claims 1 or 2, wherein the amount of L_1 is at least 40 wt% and the weight ratio of $L_1:L_2$ is at least 3.5 are even more preferred.

The amount of saturated C_{14+} fatty acids in our fats is preferably 15-50 wt%. It was found, that fats with relatively high levels of C_{18} -saturated fatty acids could be obtained. Advantageously the level of C_{16} - C_{18} saturated fatty acids is more than 30 wt%, in particular more than 40 wt% if a good structuring fat is desired. If a healthier structuring fat is desired with better structuring properties the amount of C_{18} saturated fatty acid is more than 20 wt%, preferably more than 30 wt%.

Fats with the best structuring properties and health characteristics are obtained if the weight ratio of saturated C_{18} :saturated C_{16} fatty acid residues is > 2 .

The most abundant polyunsaturated fatty acid L_1 is preferably DHA (= $C_{22:6}$). The second most abundant polyunsaturated fatty acid L_2 advantageously is EPA ($C_{20:5}$). Very useful triglycerides are obtained, when L_1 = EPA and L_2 = DHA.

Our triglycerides can be applied as such in foodproducts, however it can also be very suitable to blend our novel fats first, before applying them. Therefore part of our invention is also a blend of triglycerides, comprising

- 0.3 - 95 wt% of triglycerides according to claims 1 - 9, and
- 99.7 - 5 wt% of a complementary fat, having a solid fat index at 10°C (N_{10}) that is either at least 5% more, or at least 5% less than the N_{10} of the triglycerides according to claims 1 - 9.

Above blends suitably can be composed of 5-80 wt%, in particular 20-70 wt% of the triglycerides according to claims 1 - 9, and 95-20 wt%, in particular 80-30 wt% of the complementary fat.

Many types of complementary fat could be applied. However we prefer to use a complementary fat that has a solid fat content (NMR-pulse; not stabilized) of more than 15 at 20°C , preferably more than 20.

Very useful complementary fats for our blends can be selected from cocoa butter equivalents, cocoa butter, palm oil or fractions thereof, palmkernel oil or fractions thereof, interesterified mixtures of above fats or fractions or hardened components thereof, or from liquid oils, such as sunflower oil, high oleic sunflower oil, soyabean oil, rapeseed oil, cottonseed oil, safflower oil, high oleic safflower oil, maize oil, MCT oils, or fish oils.

The blends so obtained display a solid fat content (NMR-pulse; not stabilized) of 0-85, preferably 10 - 70, most preferably 20 - 60 at 5°C and less than 30, preferably < 20 , most preferably < 5 at 35°C .

Although our fats already have acceptable oxidative stabilities stability we found that this stability can be further improved when our blends contain an effective amount of an oxidation stabilizer, selected from the group consisting of: natural or synthetic tocopherols, other natural anti-oxidants, BHT, BHA, free radical scavengers, enzymes with anti-oxidant properties. Effective amounts can range from 100 ppm to 5 wt% (on fat).

Part of our invention are also the foodproducts, comprising a fat phase, in particular spreads and margarine. However our fats can also be used in cream alternative, infant food, chocolate, confectionery, bakery products, sauces, ice-

creams, ice-cream coatings, cheese, soups, mayonnaise, dressings, enteral or parental products, wherein the fat phase contains a fat according to claims 1 - 15.

Our fats can be obtained by preparing the pure triglycerides and blending these in the required ratios.

However a very useful method for the preparation of our blends is an interesterification of a (non-hardened) fish oil with a saturated fatty acid. This interesterification can be performed by using an enzyme. In that case enzymes can be applied, that display a specificity for e.g. long chain polyunsaturated fatty acids over saturated fatty acids, or that display a preference for one long chain polyunsaturated fatty acid over another long chain polyunsaturated fatty acid.

In our example we have set out another possible interesterification method for the preparation of our novel fats. According to this method a fish oil is first subjected to glycerolysis in the presence of a lipase. The crude reaction product obtained is enriched in long chain polyunsaturated fatty acids. This crude product is reconverted to triglycerides by performing an interesterification, using a fat high in e.g. C₁₆ or C₁₈ saturated fatty acids, such as hardened low erucic rape seed oil. Other routes for the preparation of our fats are illustrated by the other examples.

LIST OF USED CODES AND THEIR EXPLANATION

w(TUNA)f = TUNAf =	The olein fraction of semi refined tuna oil obtained low temperature solvent fractionation, having at least 35 % of DHA.
BO68 =	Hardened soyabean oil melting point 68°C.
POs =	Dry fractionated palm oil stearine fraction.
CCB =	Cocoa butter.
POf37 =	Partially hardened palm oil olein fraction melting point of 37°C.
CN =	Coconut oil.
CNs =	Coconut oil stearin fraction.
nPOm =	Wet fractionated palm oil mid fraction.
df(PO)f =	Dry fractionated palm oil olein fraction.
HS1 = Hardstock =	The stearin fraction of a chemical interesterified blend of fully hardened palm oil and a fully hardened palm kernel olein fraction.
SF =	Sunflower oil.
PO =	Palm oil.
in =	Intesterified.

EXAMPLE I

A fish oil enriched in 20:5 and 22:6 is prepared by reacting menhaden oil (composition given in table 1.) with glycerol in the presence of *Pseudomonas cepacia* lipase at a temperature of 37°C. The ratio of oil to glycerol is 3 (wt/wt) and the quantity of lipase is 1% by weight on oil. 5% water by weight is present in the glycerol. After 48 hours the reaction is terminated by heating to 100°C and the glycerol is separated from the reaction mixture. The triglycerides are separated from the glyceride fraction by adsorption of the partial glycerides and the free fatty acids (FFA) onto silica, to give the enriched oil of composition shown in table 1. This oil is interesterified with hardened low erucic acid rapeseed oil (composition in table 1.) using *Rhizomucor miehei*, to give the final product oil with a composition given in table 1. All the above processes are carried out under nitrogen to prevent deterioration of the oil.

Table 1. Fatty acid composition (wt%).

	C14:0	C16:0	C16:1	C16:n	C18:0	C18:1	C18:2	C18:3	C18:4	C20:0	C20:1	C20:5	C20:n	C22:0	C22:1	C22:5	C22:6	C22:n	C24:0
Original oil	8.3	19.6	11.9	6.5	3.4	12.4	1.3	1.5	2.5	0.8	0.3	14.5	3.6	0.0	0.3	2.5	6.5	1.3	0.0
Enriched oil	0.3	4.3	6.7	3.8	1.5	16.9	1.8	1.7	3.5	1.0	2.8	28.1	6.8	0.0	0.0	5.6	13.6	1.9	0.0
Hardened low erotic acid impacted oil (LEAR oil)	0.0	4.0	0.0	0.0	94.0	0.0	0.0	0.0	0.0	2.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
75% enriched fish oil + 25% hardened LEAR oil	0.2	4.2	5.0	2.8	24.6	12.7	1.3	1.3	2.6	1.3	2.1	21.1	5.1	0.0	0.0	4.2	10.2	1.4	0.0

EXAMPLE II

A low temperature solvent fractionation at -70°C was done on semi refined tuna oil with the composition, mentioned in table II, under the conditions as mentioned in "Progress in the chemistry of fats and other lipids" vol. 3 Holman R.T. et al 1955, using 4 L of acetone per Kg tuna oil to enrich the oil in DHA and EPA. After removal of the acetone the olein fraction of the tuna oil ($= \text{wt(tuna)l}$) with the composition, mentioned in table 2, was obtained. This fraction was stored in the freezer under nitrogen.

All the ingredients for the enzymic interesterification were stored at ambient for at least one hour. All oils were used as liquid oils. To the tuna oil olein fraction 400 ppm of anti-oxidant (BHT) was added.

The tuna oil olein fraction was divided in different portions. Then the liquid complementary fat was added to each of the tuna oil olein fractions and mixed in. A sample was taken for carbon number and FAME analyses. For the enzymic interesterification a 1,3 specific lipase (*Rhizomucor Miehe*) was used. The lipase was added to the mixed oils in a weight ratio of 40:1 oil:lipase. A nitrogen blanket was put over the mixture to prevent deterioration of the oil. The reaction mixture was put in a magnetic stirred heatblock and the temperature was adjusted to 60°C . After 96 hours the reaction was stopped.

The samples were cleaned through an alumina column to remove FFA, mono- and diglycerides. Carbon number and FAME analyses were done via GC on the samples before and after lipase treatment.

Two methods were used to prove that at least 5% of the total amount of C14+ was bonded on a triglyceride molecule with L1 and/or L2. The first method involves a calculation and gives the maximum amount which is bonded on a triglyceride molecule with L1 and / or L2. The second method which involves an analytical method gives some information about the minimum amount which is bonded on the same triglyceride molecule with L1 and / or L2.

A statistical program was used to calculate a carbon number based on the randomized distribution of the fatty acids in a triglyceride molecule. This program was checked by using the FAME results of a (random) chemical interesterification for a standard interesterified fat mix from palm oil stearin/palm kernel stearin and comparing the calculated carbon number profile with the measured carbon number profile (see table 3). The differences were very small so that it was concluded that the program gives the correct results. Then the enzymic interesterification according to the invention was tested. The FAME and carbon number of the enzymic interesterified product were measured. The measured carbon number was equated to the calculated carbon number and the differences were very small. Because of this we concluded that the enzymic interesterification resulted in a random distribution of the fatty acids in the triglyceride molecule. In a randomized interesterified product it is possible to calculate the amount of C14+ bonded on a triglyceride molecule with L1 and/or L2.

The second method is an analytical method. Two parts of the sample (Band a and Band b) with a certain amount of unsaturation were collected by using Silver-ion HPLC. Band A had about 6 till 9 unsaturations and Band B had 9 till 18 unsaturations. On the triglycerides of the two bands FAME and carbon number analyses were done.

From these FAME analyses a carbon number was calculated by using the statistical program. This carbon number was equated to the measured carbon number. From these analyses and calculations it was possible to calculate the minimum amount of C14+ which was bonded on a triglyceride molecule with L1 and/or L2. The actual amount will be even higher because there was more sample than just the two analyzed bands.

Intesterification experiments were done on the following blends:

70/20/5	wt(tuna)l / BO68 / POs
70/20/5	wt(tuna)l / POs / BO68 (= comparative example)

The composition of BO68 and POs are given in table 2.

The experiments were done according to the method described above. The experiments were stopped after 96 hours. The carbon number and FAME of the blends and the interesterified blends were determined. The results of the FAME analyses are listed in table 4 and the results of the carbon number analyses are listed in table 5.

The results of the calculated amount of C14+ which is bonded on a triglyceride molecule with L1 and/or L2 are listed in table 6. The results of the analyzed amount of C14+ which is bonded on a triglyceride molecule with L1 and/or L2 are listed in table 7.

EXAMPLE III

Intesterification experiments were done on the following blends:

75/25	wt(tuna)l / BO68
75/25	wt(tuna)l / POs (comparative example)

The BO68 and POs are the same as in example II (see table 2).

The experiments were done according to the method described in example II. This tuna olein fraction was alumina treated to remove FFA, mono- and diglycerides, before lipase treatment. After 96 hours the experiments were stopped. The analyses of the reaction mixtures were done. The results of all these analyses are listed in tables 8 and 9.

The results of the calculated amount of C14+ which is bonded on a triglyceride molecule with L1 and/or L2 are listed in table 10. The results of the analyzed amount of C14+ which is bonded on a triglyceride molecule with L1 and/or L2 are listed in table 11.

Unstabilised N-values were measured on the reaction products as well. These were:

	in(wf(TUNA)/BO68)	in(wf(TUNA)/POs)
N-10 n.s.	14.4 %	8.8 %
N-20 n.s.	9.0 %	6.9 %
N-30 n.s.	4.6 %	3.9 %

EXAMPLE IV

A fish oil concentrate was made according to the following procedure.

1. Chemical Hydrolysis of Tuna oil

Method adapted from Ratnayake et al (Fat Sci. Tech. 90 (10), 1988, page 381)

Tuna oil (200g) was refluxed for 1 hour in an atmosphere of nitrogen with a mixture of 47 g of potassium hydroxide pellets, 260 ml ethanol (96%), and 88 ml deionised water. The saponified mixture was diluted with 500 ml of water and the non-saponifiable matter was extracted with hexane (3 x 100ml). The aqueous layer was neutralised with 500ml of 1 M HCl. The free fatty acids were extracted into hexane (3x 100ml). The hexane was removed by evaporation.

2. Urea Fractionation of Tuna Acids

Method adapted from Robles Medina et al JAOCS vol 72 no 5 (1995)

The fatty acids (100g) were added with stirring to a hot (60°C) solution of 400g of Urea and 800 ml of ethanol. The mixture was stirred for 1 hour before the temperature was reduced by 1°C/hour to 4°C at which temperature the mixture was held for 16 hours. The mixture was fractionated to remove the stearin fraction. The ethanol was removed from the olein fraction by evaporation. The olein was mixed with 250 ml of hexane and 250 ml of 1 M HCl. The hexane layer was isolated and the aqueous layer washed with a further 100 ml hexane. The hexane was removed by evaporation.

3. Recombination to triglyceride batch 1

47 g of Tuna acids were mixed with approximately 4 g of glycerol and 4 g of *Rhizomucor miehei* in a jacketed vessel at 55°C with a magnetic stirrer. Nitrogen was allowed to blow over the surface to remove any water produced during the reaction. The reaction was allowed to continue for 10 days until the FFA had been substantially reduced. The product after removal of the enzyme by filtration was stirred at 60°C with 50 g of basic alumina in 100 ml of hexane. The alumina was removed by filtration.

batch 2

The free fatty acids were divided into 4 samples which were recombined to triglyceride on 12 to 15 g scale in glass vials at 55°C in a magnetic hot block. Typically 14 g of free fatty acid were mixed with 1.3 g glycerol and 0.7 g *Rhizomucor miehei*. Nitrogen was allowed to flow over the surface to remove water. The reactions were allowed to continue for 1 week. 50 g of product, after removal of the enzyme by filtration, was stirred at 60°C with 270 g of basic alumina in 100 ml of hexane. The alumina was removed by filtration.

The oil from "Recombination to triglycerides" batch 1 was called D58. The FAME composition of D58 is given in table 12.

Interesterification experiment was done on the following blend:

75/25 fish oil concentrate (= D58) / BO68

The interesterification experiment was done according to the method of example II.

The interesterification experiment was stopped after 115 hours. The FAME and carbon number analysis were done, the results are listed in table 12 and 13.

The results of the calculated amount C14+ which is bonded on a triglyceride molecule with L1 and/or L2 of this sample is listed in table 14.

EXAMPLE V

The interesterification experiments were done according to the method of example II. This time the interesterification reactions were stopped after 46 hours.

The following interesterified blend was used :

75 / 25 wf(TUNA) / BO68

The FAME and carbon numbers of this interesterified mixture are listed in table 15 and 16.

D40 being a tuna oil olein fraction, obtained by low temperature solvent fractionation, having about 38 wt % of DHA.

EXAMPLE VI

Blends were made of the interesterified mixture mentioned in example V (= in(FISH)) and a complementary fat / fat blend for the following applications:

Application	Reference	Blend inside the patent
Chocolate	Cocoa butter	Cocoa butter/in(FISH) 99/1
Bakery	PO137/dl(PO)l 40/60	PO137/dl(PO)l/in(FISH) 40/50/10
Ice cream coatings	Coconut oil	CN/CNs/in(FISH) 90/5/5
Ice cream	PO	PO/in(FISH) 90/10
Non dairy creams	nPOm/dl(PO)l 40/60	nPOm/dl(PO)l/in(FISH) 40/40/20
Health margarines / Health spreads	HS1/SF 13/87	HS1/SF/in(FISH) 13/77/10
Confectionery fillings	nPOm/dl(PO)l 60/40	nPOm/dl(PO)l/in(FISH) 60/20/20
Mayonnaise / Sauces	SF	SF/in(FISH) 90/10
Dressings	SF	SF/in(FISH) 90/10

The range of N-values of the references and measured N-values for the blends are listed in table 17.

EXAMPLE VII

The interesterification experiments were done according to the method of example II. This time the interesterification reactions were stopped after 48 hours.

The two following interesterified blends were used :

75 / 25 wf(TUNA) / BO68

75 / 25 wf(TUNA) / POs

The FAME and carbon numbers of these interesterified mixture are listed in table 18 and 19.

EXAMPLE VIII

Spreads were made according to the following recipe:

Fat Phase	
Fat Blend	40 %
Hymono 7804	0.3 %
Colour (2% b-carotene)	0.02 %
Total Water	40.32 %

Aqueous Phase (to pH 5.1)	
Water	56.44 %
Skimmed Milk Powder	1.5 %
Gelatin (270 bloom)	1.5 %
Potassium Sorbate	0.15 %
Citric Acid Powder	0.07 %
Total	59.66 %

In above recipe two different fat blends were applied. The fat blend according to the invention was as follows: - example VII in(wf(TUNA)/BO68) according to

The fat blend used as comparative example was as follows: in(wf(TUNA)/t/POs)

The FAME results of the in(wf(TUNA)/t/BO68) and the in(wf(TUNA)/t/POs) are listed in table 18.

The spreads were processed according to the following procedure:

2 kg of material was prepared and processed.

A micro-votator processing line was set up as follows:

- Premix conditions
 - Stirrer Speed 60 rpm
 - Temperature 50°C
- pump
 - Proportioning pump set at 60% (30 g/min.).
- A₁ conditions
 - Shaft speed 1000 rpm
 - Temperature set at 2°C
- C₁ conditions
 - Shaft speed 1000 rpm
 - Temperature set to 8°C
- A₂ conditions
 - Shaft Speed 1000 rpm
 - Temperature set to 0°C
- C₂ conditions
 - Shaft speed 1000 rpm
 - Temperature set to 8°C

The aqueous phase was prepared by heating the required amount of water to approximately 80°C and then, using a Silverson mixer, slowly mixing in the ingredients. The pH of the system was adjusted to 5.1 by adding 20% Lactic acid solution as required.

A premix was prepared by stirring the fat phase in the premix tank and then slowly adding in the aqueous phase. When addition was complete, the mix was stirred for a further 5 minutes before pumping through the line. When the process had stabilised (around 20 minutes), product was collected for storage and evaluation.

The process conditions for the spread of in(wf(TUNA)/BO68) were as follows:

Sample	A ₁ Exit (°C)	C ₁ Exit (°C)	A ₂ Exit (°C)	C ₂ Exit (°C)	Line Pressure (bar)
in(wf(TUNA)/ BO68)	9.9	16.7	8.2	13.1	1.3 to 1.6

Under these conditions a good oil continues low fat spread was produced.

A comparative spread using in(wf(TUNA)/POs) was attempted under the same conditions as those above. This could not be achieved using these conditions.

In order to achieve a good oil continues low fat spread, the votator had to be altered to the following conditions:

pump - Proportioning pump set at 40% (20 g/min.).

A₁ conditions - Shaft speed 1000 rpm
- Temperature set at -7°C

C₁ conditions - Shaft speed 1000 rpm
- Temperature set to 4°C

A₂ conditions - Shaft Speed 1000 rpm
- Temperature set to -7°C

C₂ conditions - Shaft speed 1000 rpm
- Temperature set to 4°C

Using these unit temperatures produced the following exit temperatures:

Sample	A ₁ Exit (°C)	C ₁ Exit (°C)	A ₂ Exit (°C)	C ₂ Exit (°C)	Line Pressure (bar)
in(wf(TUNA)/POs)	4.3	12.5	3.0	10.2	1.4 to 2.7

Evaluations were done on C-value and on conductivity. The C-value in g/cm² of the spreads was measured by using a cone penetrometer. The conductivity in μ siemens/cm was measured by using a Wayne Kerr.

	5°C
Sample	C-value
in(wf(TUNA)/BO68)	440
in(wf(TUNA)/POs)	< 90

The spread made with in(wf(TUNA)/POs) was too soft to enable us to measure a C-value.

EXAMPLE IX

Range style dressings were made according to the following recipe:

	wt%
Liquid oil	25.0
Maltodextrin	20.0
Dried egg yolk	0.8
Xanthum gum	0.4
Vinegar	5.0
Water	44.8

In above recipe two different liquid oils were applied. The liquid oil for the reference was Sunflower oil and the liquid oil according to the invention was as follows:

- Sunflower oil / in(D40/BO68) 90/10

The FAME results of the in(D40/BO68) are listed in table 15. Results of the NMR measurements of the blend according to the invention are listed in table 17.

A large batch of aqueous phase was manufactured and used for all the dressings. The water and maltodextrin were first blended using a Silverson mixer. The egg yolk, xanthum gum and vinegar were sequentially added whilst continuing to stir with the Silverson until complete mixing had occurred. At this stage the pH = 3.25, therefore no further adjustment to the pH was made.

The oils were slowly added to the aqueous phase whilst mixing using the Silverson. Mixing was continued until all the oil had been dispersed. The dressings were transferred to 200 ml plastic sterile bottles.

The viscosities of the samples were determined using a Brookfield Viscometer fitted with a number 4 spindle rotating at 10 rpm. The samples were contained in identical 200 ml plastic bottles hence the viscosities are directly comparable with each other. For each sample the average of three measurements was taken with the sample being allowed to relax for 1 minute between each 1 minute of shear. The viscosity results of the dressings are listed in table 20.

The oil droplet size distribution was determined using a Malvern Mastersizer using a 45 mm filter. The results of these measurements, as Sauter-mean particle diameter are listed in table 20.

EXAMPLE X

Spreads were made according to the following recipe:

Fat Phase	
Fat Blend	40 %
Hymono 7804	0.3 %
Colour (2% b-carotene)	0.02 %
Total Water	40.32 %

Aqueous Phase (to pH 5.1)	
Water	58.44 %
Skimmed Milk Powder	1.5 %
Gelatin (270 bloom)	1.5 %
Potassium Sorbate	0.15 %
Citric Acid Powder	0.07 %
Total	59.66 %

In above recipe two different fat blends were applied. The fat blend for the reference was HS1 / Sunflower oil 13/87 and the fat blend according to the invention was as follows:

- HS1 / Sunflower oil / in(D40/BO68) 13/77/10

The FAME results of the in(D40/BO68) are listed in table 15. Results of the NMR measurements of the blend according to the invention are listed in table 17.

The spreads were processed according to the following procedure:
2 kg of material was prepared and processed.

A micro-votator processing line was set up as follows:

Premix conditions - Stirrer Speed 60 rpm

- Temperature 50°C

pump - Proportioning pump set at 60% (30 g/min.).

A₁ conditions - Shaft speed 1000 rpm

- Temperature set at 8°C

C₁ conditions - Shaft speed 1000 rpm

- Temperature set to 10°C

A₂ conditions - Shaft Speed 1000 rpm

- Temperature set to 10°C

C₂ conditions - Shaft speed 1000 rpm

- Temperature set to 13°C

The aqueous phase was prepared by heating the required amount of water to approximately 80°C and then, using a silicon mixer, slowly mixing in the ingredients. The pH of the system was adjusted to 5.1 by adding 20% Lactic acid solution as required.

A premix was prepared by stirring the fat phase in the premix tank and then slowly adding in the aqueous phase. When addition was complete, the mix was stirred for a further 5 minutes before pumping through the line. When the process had stabilised (around 20 minutes), product was collected for storage and evaluation.

The typical process conditions were as follows:

Sample	A ₁ Exit (°C)	C ₁ Exit (°C)	A ₂ Exit (°C)	C ₂ Exit (°C)	Line Pressure (bar)
Reference	13.2	18.7	13.6	15.6	0.5 to 2
HS1/SF/in(D40/BO68) 13/77/10	12.2	18.6	13.4	15.0	1 to 3

For both systems, very good oil continuous low fat spreads were produced using this system.

Evaluations were done on C-value and on conductivity. The C-value in g/cm² of the spreads was measured by using a cone penetrometer. The conductivity in μ siemens/cm was measured by using a Wayne Kerr.

Sample	20°C	
	C-value	Conductivity
Reference	190	10 ⁻⁵
HS1/SF/m(D40/BO68)	130	10 ⁻⁵

All samples spread very easily on grease-proof paper, with no obvious signs of water loss

EXAMPLE XI

Ice cream was made according to the following recipe:

	wt%
Fat blend	10.0
Skimmed milk powder	10.0
Icing sugar	12.0
Corn syrup solids	4.0
Dextrose monohydrate	2.0
Sherex IC 9330®	0.6
Water	61.4
Total	100.0

Sherex IC 9330® is a product from Quest International and comprises mono- and diglycerides admixed with different stabilizers.

In above recipe two different fat blends were applied. The fat blend for the reference was PO / Sunflower oil 90/10 and the fat blend according to the invention was as follows:

- PO / in(D40/BO68) 90/10

The FAME results of the in(D40/BO68) are listed in table 15. Results of the NMR measurements of the blend according to the invention are listed in table 17.

All ingredients except the water and the fat were mixed. Then the cold water was added to this mixture. This mixture was heated in a water bath till a temperature of 70°C. Then the fully liquid palm oil was added to the mixture while "stirred" in the ultra-turrax. This emulsion was cooled in a water bath at 20°C until a temperature of 30°C was reached. The emulsion was stirred in the ultra-turrax again.

The batch ice cream machine was held for 24 hours at -28°C prior to use. The emulsion was placed in the batch ice cream machine and stirred for 15 minutes. The resulting ice cream was stored at -20°C for 24 hours and then evaluated.

The viscosity of the ice cream emulsion, prior to freezing was measured. The overrun and hardness were determined. The viscosity was measured by using the Haake viscometer. Hardness was measured by using a Stevens texture analyser with a 45° cone at a speed of 0.5 mm/second till a depth of 2 mm.

Sample	Overrun (%)	Hardness (gram)
Reference	31.5	142
PO/in(D40/BO68)	42.7	141.4

The viscosities of the emulsions were similar.

Table 2

FAME data for the components used				
FAME	Semi refined tuna oil	wt(TUNA)†	BO68	POs
C12:0	0.0	0.0	0.1	0.0
C12:other	0.0	4.0	0.0	0.0
C14:0	3.5	1.7	0.2	0.8
C14:other	0.0	4.0	0.0	0.0
C16:0	20.8	3.1	13.8	91.8
C16:1	0.0	7.6	0.0	0.1
C16:others	0.0	3.2	0.2	0.1
C18:0	0.0	4.0	83.7	3.8
C18:1	14.8	16.1	0.8	2.6
C18:2	1.2	3.1	0.1	0.0
C18:3	0.0	4.0	0.0	0.0
C18:others	0.0	1.7	0.0	0.0
C20:0	0.0	4.0	0.6	0.0
C20:1	1.1	1.1	0.0	0.0
C20:2	0.0	0.0	0.0	0.0
C20:3	0.0	4.0	0.0	0.0
C20:4	0.0	4.0	0.0	0.0
C20:5	5.1	12.0	0.0	0.0
C20:others	3.1	4.0	0.0	0.0
C22:0	0.0	0.0	0.0	0.0
C22:1	0.3	4.0	0.0	0.0
C22:2	0.0	2.1	0.0	0.0
C22:3	24.8	39.6	0.0	0.0
C22:others	2.9	2.8	0.0	0.0
C24:0	0.0	4.0	0.1	0.0
others	0.0	0.0	0.0	0.0
Total	100.0	100.0	99.9	100.0

Table 3

Programm check on a chemical intersterification			
	wfPOs/PKs (blend)	in(wfPOs/PKs)	Calculated bystatistical program
FAME			
C8:0 (%)	0.6	0.6	
C10:0 (%)	4.1	1.1	
C12:0 (%)	22.5	22.5	
C14:0 (%)	10.0	9.9	
C16:0 (%)	50.2	50.5	
C17:0 (%)	0.1	0.4	
C18:0 (%)	4.3	4.3	
C18:1 (%)	9.9	10.0	
C18:2 (%)	0.6	0.4	
C20:0 (%)	0.3	0.3	
C22:0 (%)	0.1	0.0	
Carbon number			
C28	4.1	0.0	0.0
C30	0.2	0.0	0.4
C32	1.4	0.4	0.2
C34	2.7	0.4	0.4
C36	11.5	3.3	2.5
C38	10.4	4.2	3.4
C40	6.4	12.7	11.4
C42	4.1	12.3	11.7
C44	2.4	21.9	22.1
C46	3.7	17.0	17.8
C48	30.5	15.5	17.0
C50	21.7	9.0	10.2
C52	3.8	2.5	2.9
C54	1.1	0.4	0.3
C56	0.1	0.1	0.0
C58	0.1	0.0	0.0

Table 4

FAME data for example II				
FAME	TUNAl / BO68 (blend)	in(TUNAl / BO68)	TUNAl / POs (blend)	in(TUNAl / POs)
C12:0	0.1	0.1	0.0	0.0
C12:other	0.0	0.0	0.0	0.0
C14:0	1.5	1.6	1.7	1.8
C14:other	0.5	0.5	0.6	0.4
C16:0	14.8	14.9	34.9	35.3
C16:1	4.4	4.7	4.3	4.9
C16:other	2.4	2.6	2.3	2.5
C18:0	26.6	27.1	7.3	7.7
C18:1	10.4	11.3	10.5	11.9
C18:2	1.2	1.1	0.5	2.1
C18:3	1.6	0.6	0.6	0.5
C18:other	1.6	1.5	0.8	0.8
C20:0	0.2	0.2	0.1	0.1
C20:1	0.7	0.8	0.8	1.3
C20:2	0.3	0.3	0.2	0.2
C20:3	1.2	0.2	0.2	2.1
C20:4	1.6	0.6	1.5	1.5
C20:5	6.3	5.8	6.2	5.5
C20:other	1.6	0.6	0.6	0.6
C22:0	0.1	0.1	0.1	1.5
C22:1	0.1	0.3	1.9	0.1
C22:5	1.2	1.1	1.2	1.1
C22:6	23.0	21.5	21.9	19.3
C22:other	1.7	1.7	1.9	1.7
C24:0	0.0	0.6	0.6	0.0
Total	100.3	99.8	99.9	100.0

Table 5

Carbon number data for example II

Carbon number	TUNAI/BO68/POs 70/20/5 (blend)	in(TUNAI/BO68/POs) 70/20/5	TUNAI/POs/BO68 70/20/5 (blend)	in(TUNAI/POs/BO68) 70/20/5
C36	0.2	0.2	0.3	0.0
C38	0.3	0.3	0.0	0.0
C40	0.4	0.3	0.3	0.0
C42	0.8	0.8	0.0	0.0
C44	0.7	0.8	0.0	0.0
C46	0.0	1.3	0.8	1.5
C48	7.9	4.3	26.6	12.3
C50	6.2	10.9	5.7	15.0
C52	14.3	18.0	5.9	14.8
C54	27.9	19.6	11.8	16.3
C56	11.9	17.0	10.3	12.6
C58	11.3	12.7	12.0	9.4
C60	10.0	8.1	12.9	10.2
C62	6.1	5.2	14.0	7.9
C64	1.0	0.7	0.0	0.0
C66	0.0	0.0	0.0	0.0
C68	0.0	0.0	0.0	0.0
Total	100.0	100.0	100.0	100.0

Table 6 Calculated data for example II of the amount of c14+ which are bonded on a triglyceride molecule with L1 and/or L2.

70/20/5 wf(tuna)f / BO68 / POs

Carbon number	Analyzed (wt%)	Calculated (wt%)	M/P/S + X (wt%) + L1/L2	M/P/S + M/P/S (wt%) + L1/L2	M/P/S wt%	wt% of the total added amount c14+ bonded on a molecule with L1 and/or L2
C36	0.2	0.0	0.0	0.0	0.0	0.0
C38	0.3	0.0	0.0	0.0	0.0	0.0
C40	0.3	0.0	0.0	0.0	0.0	0.0
C42	0.6	0.0	0.0	0.0	0.0	0.0
C44	0.8	0.1	0.0	0.0	0.0	0.0
C46	1.3	0.6	0.0	0.0	0.0	0.0
C48	4.3	3.0	0.0	0.0	0.0	0.0
C50	10.9	8.9	0.0	0.0	0.0	0.0
C52	18.0	15.6	0.6	1.0	0.8	1.8
C54	19.6	18.1	3.6	3.6	3.3	7.5
C56	17.0	19.2	6.2	6.3	5.8	13.2
C58	12.7	16.2	6.6	4.4	4.8	11.0
C60	8.1	8.8	5.4	0.0	1.5	3.5
C62	5.2	7.0	4.1	0.0	1.2	2.7
C64	0.7	2.4	0.0	0.0	0.0	0.0
C66	0.0	1.2	0.0	0.0	0.0	0.0
Total	100.0	100.1			0.0	35.8

x = all fatty acids except M, P and S (C14:0, C16:0 and C18:0)

/ = or

Table 7

Analyzed results of example II of the amount of C14+ which are bonded on a triglyceride molecule with L1 and/or L2							
	HPLC band	Band as % TAGS (g/100g)	Sum of Cno's containing target TAG in band (%wt)	Sum of target acids in band (%wt)	Target acids in target TAGs in band (g/100g)	Target acids in total FAME on TG (%wt)	Therefore target acids in target TAGs(%wt on total FAME)
in(TUNAF BO68/POs 70/20/5	A	31.7	96.0	44.0	13.4	43.6	30.7
	B	32.3	46.0	19.2	2.9	43.6	6.5
						Total:	37.3

Table 8

FAME data for example III				
FAME	TUNAI / BO68 (blend)	in(TUNAI / BO68)	TUNAI / POs (blend)	in(TUNAI / POs)
C12:0	0.1	0.1	0.1	0.1
C12:other	0.1	0.1	0.1	0.0
C14:0	1.3	1.3	1.5	1.6
C14:other	0.5	0.5	0.5	0.5
C16:0	5.0	5.2	26.8	30.0
C16:1	5.3	5.3	5.3	5.7
C16:other	2.6	2.6	2.5	2.7
C18:0	21.8	23.3	1.2	1.3
C18:1	12.6	12.5	12.3	13.3
C18:2	1.4	1.4	1.5	1.5
C18:3	0.8	0.8	0.8	0.8
C18:other	2.1	2.0	2.1	1.8
C20:0	0.1	0.1	0.0	0.1
C20:1	0.7	0.7	0.7	0.8
C20:2	0.2	0.2	0.2	0.2
C20:3	0.2	0.2	0.2	0.2
C20:4	2.0	1.9	1.9	1.8
C20:5	8.6	8.2	8.5	7.6
C20:other	1.0	0.9	0.9	0.8
C22:0	0.1	0.1	0.0	0.0
C22:1	0.2	0.2	0.2	0.2
C22:5	1.4	1.4	1.4	1.3
C22:6	30.0	29.1	29.5	26.0
C22:other	2.0	1.9	1.9	1.7
C24:0	0.0	0.0	0.0	0.0
Total	99.8	100.0	100.1	100.0

Table 9

Carbon number data for example iii

Carbon number	TUNAI / BO68 (blend)	in(TUNAI / BO68)	TUNAI / POs (blend)	in(TUNAI / POs)
C38	0.0	0.1	0.0	0.0
C40	0.0	0.1	0.0	0.2
C42	0.1	0.2	0.0	0.3
C44	0.2	0.4	0.3	0.6
C46	0.4	0.9	1.5	2.1
C48	1.0	2.0	24.4	12.3
C50	3.7	5.3	5.6	13.8
C52	12.5	12.3	5.2	12.7
C54	26.1	18.0	8.1	14.7
C56	13.1	18.1	12.4	13.4
C58	15.4	16.7	14.5	10.8
C60	13.8	12.3	13.4	11.2
C62	9.4	10.2	10.4	5.6
C64	3.3	2.8	3.3	2.0
C66	1.0	0.6	0.9	0.3
C68	0.0	0.0	0.0	0.0
Total	100.0	100.0	100.1	100.0

Table 10 Calculated data of example III of the amount of C14+ which are bonded on a triglyceride molecule with L1 and/or L2.

75/25 wf(tuna)f / B068

Carbon number	Analyzed (wt%)	Calculated (wt%)	M/P/S + X (wt%) + L1/L2	M/P/S + M/P/S(wt%) + L1/L2	M/P/S wt%	wt% of the total added amount c14+ bonded on a molecule with L1 and/or L2
C36	0.0	0.0	0.0	0.0	0.0	0.0
C38	0.1	0.0	0.0	0.0	0.0	0.0
C40	0.1	0.0	0.0	0.0	0.0	0.0
C42	0.2	0.0	0.0	0.0	0.0	0.0
C44	0.4	0.0	0.0	0.0	0.0	0.0
C46	0.9	0.3	0.0	0.0	0.0	0.0
C48	2.0	1.2	0.0	0.0	0.0	0.0
C50	5.3	4.0	0.0	0.0	0.0	0.0
C52	12.3	9.3	0.3	0.4	0.3	1.1
C54	18.0	14.7	2.5	1.3	1.6	5.2
C56	18.1	17.9	6.6	3.7	4.3	14.6
C58	16.7	20.8	8.9	4.6	5.6	18.7
C60	12.3	13.1	6.0	0.0	1.8	5.9
C62	10.2	12.7	6.4	0.0	1.9	6.2
C64	2.8	3.3	0.0	0.0	0.0	0.0
C66	0.6	2.8	0.0	0.0	0.0	0.0
Total	100.0	100.1				51.7

x = all fatty acids except M, P and S (C14:0, C16:0 and C18:0)

/ = or

Table 11

Analyzed results of example III of the amount of C14+ which are bonded on a triglyceride molecule with L1 and/or L2.							
	HPLC band	Band as % TAGs (g/100g)	Sum of Cno's containing target TAG in band (%wt)	Sum of target acids in band (%wt)	Target acids in target TAGs in band (g/100g)	Target acids in total FAME on TG (%wt)	Therefore target acids in target TAGs(%wt on total FAME)
in(TUNAF BO68/POs)	A	31.9	74.4	30.2	7.2	28.7	25.0
	B	38.4	49.0	10.8	2.0	28.7	7.1
						Total:	32.1

Table 12

FAME data for example IV		
FAME	D58	in(D58 / BO68)
C14:0	0.1	0.1
C14:other	0.5	0.3
C18:0	0.1	3.6
C16:1	1.0	0.7
C16:other	3.4	2.4
C18:0	0.2	26.8
C18:1	0.9	1.5
C18:2	1.8	1.4
C18:3	0.8	0.1
C18:other	3.5	2.3
C20:0	0.0	0.2
C20:1	0.1	0.0
C20:2	0.0	0.0
C20:3	0.4	0.4
C20:4	4.6	3.3
C20:5	16.1	10.8
C20:other	1.4	1.1
C22:0	0.0	0.1
C22:1	0.1	0.0
C22:5	2.0	1.4
C22:6	27.3	39.3
C22:other	5.6	3.8
C24:0	0.0	0.0
Total	99.9	100.0

Table 13

Carbon number data for example IV		
Carbon number	D58/BO68 (blend)	ln(D58/BO68)
C36	0.0	0.6
C38	0.0	1.7
C40	0.0	1.9
C42	0.6	3.3
C44	1.5	1.8
C46	0.9	1.9
C48	0.0	0.7
C50	3.7	2.3
C52	14.4	5.0
C54	32.2	10.7
C56	5.2	14.7
C58	7.3	19.9
C60	10.8	14.7
C62	10.3	12.6
C64	7.3	5.5
C66	3.8	0.6
C68	0.0	0.0
Total	100.0	100.0

Table 14 Calculated data of example IV of the amount of C14+ which are bonded on a triglyceride molecule with L1 and/or L2.

75/25 fish oil concentrate (= D58) / B068

Carbon number	Analyzed (wt%)	Calculated (wt%)	M/P/S + X (wt%) + L1/L2	M/P/S + M/P/S(wt%) + L1/L2	M/P/S wt%	wt% of the total added amount c14+ bonded on a molecule with L1 and/or L2
C32	0.0	0.0	0.0	0.0	0.0	0.0
C34	0.0	0.0	0.0	0.0	0.0	0.0
C36	0.6	0.0	0.0	0.0	0.0	0.0
C38	1.7	0.0	0.0	0.0	0.0	0.0
C40	1.9	0.0	0.0	0.0	0.0	0.0
C42	3.3	0.0	0.0	0.0	0.0	0.0
C44	1.8	0.0	0.0	0.0	0.0	0.0
C46	1.9	0.0	0.0	0.0	0.0	0.0
C48	0.7	0.1	0.0	0.0	0.0	0.0
C50	2.3	0.8	0.0	0.0	0.0	0.0
C52	5.0	3.1	0.0	0.0	0.0	0.0
C54	10.7	7.5	1.2	0.8	0.9	3.0
C56	14.8	12.7	3.7	4.9	4.2	14.2
C58	19.9	20.4	6.0	8.7	7.2	24.2
C60	14.7	18.0	12.2	0.0	3.6	12.1
C62	12.6	21.4	14.7	0.0	4.3	14.3
C64	5.5	8.5	0.0	0.0	0.0	0.0
C66	2.6	7.6	0.0	0.0	0.0	0.0
Total	100.0	100.1				67.8

x = all fatty acids except M, P and S (C14:0, C16:0 and C18:0)

/ = or

Table 15

FAME data for example V		
FAME	D40	in(D40 / BC68)
C12:0	0	0
C12:other	0	0
C14:0	0	2
C14:other	1	0
C16:0	7	8
C16:1	4	3
C16:other	0	2
C18:0	2	31
C18:1	16	11
C18:2	1	0
C18:3	1	0
C18:other	0	2
C20:0	0	0
C20:1	0	0
C20:2	0	0
C20:3	0	0
C20:4	0	1
C20:5	7	5
C20:other	2	0
C22:0	0	0
C22:1	3	2
C22:5	4	3
C22:6	38	26
C22:other	2	2
C24:0	0	0

Table 16

Carbon number data for example V

Carbon number	D40 / BO68 (blend)	in(D40 / BO68)
C42	0.3	0.4
C44	1.2	1.2
C46	1.7	1.9
C48	1.8	2.2
C50	4.9	6.0
C52	14.0	12.0
C54	27.9	19.0
C56	10.5	17.4
C58	10.4	19.7
C60	10.7	9.5
C62	9.0	9.2
C64	3.8	1.6
C66	3.1	0.0
C68	0.0	0.0
Total	100.0	100.1

Table 17

N-values for blends example VI					
Application	Blend	N-5 n.s. (%)	N-10 n.s. (%)	N-20 n.s. (%)	N-35 n.s. (%)
Chocolate	Typical values	85 -95	80 -95	55 -65	< 1
	99/1 CCB / in(D40/BO68)	89.7	86.2	60.3	0.0
Bakery	Typical values	40 -80	30 -75	20 -45	< 15
	40/50/10 POI87 / dfPOI / in(D40/BO68)	61.5	43.9	25.7	0.4
Ice cream coatings	Typical values	65 -90	> 35	> 15	< 1
	90/5/5 CN / CNs / in(D40/BO68)	76.4	63.2	36.0	0.1
Ice cream	Typical values	40 -60		15 -30	< 5
	90/10 PO/in(D40/BO68)	52.3		22.8	4.2
Non dairy creams	Typical values	1 - 70		0 - 37	0 - 11
	40/40/20 nPOm / dfPOI / in(D40/BO68)	55.5		15.2	0.0
Health margarine/Health spreads	Typical values	7 - 20		3 - 12	< 2.5
	13/77/10 HS1 / SF / in(D40/BO68)	18.9		11.9	2.5
Confectionery filling	Typical values	> 50	> 40	> 25	< 1.5
	60/20/20 nPOm / dfPOI / in(D40/BO68)	65.6	55.4	32.9	1.2
Mayonnaise / Sauces	Typical values	0 - 10	0 - 5	< 1	< 0.5
	90/10 SF/in(D40/BO68)	1.0	0.7	0.4	0.1
Dressings	Typical values	0 - 10	0 - 5	< 1	< 0.5
	90/10 SF/in(D40/BO68)	1.0	0.7	0.4	0.1

Table 18

FAME data for example VII.		
FAME	w(TUNA)/POs	w(TUNA)/BO68
C12:0	0.1	2.8
C14:0	1.9	1.7
C14:other	0.9	0.6
C16:0	24.7	6.9
C16:1	5.3	5.3
C18:other	2.8	2.8
C18:0	1.8	24.5
C18:1	15.1	12.8
C18:2	2.0	1.4
C18:3	0.8	0.8
C18:4	1.1	1.0
C18:other	0.9	2.8
C20:0	0.1	0.2
C20:1	0.9	0.8
C20:2	0.2	0.2
C20:3	0.8	0.2
C20:4	1.9	1.9
C20:5	6.8	6.7
C20:other	0.9	0.7
C22:0	0.0	0.1
C22:1	0.3	0.2
C22:5	1.3	1.3
C22:6	28.0	26.7
Other C22	2.5	2.3

Table 19

Carbon number data for example VII.				
Carbon Number (area%)	wt(TUNA) / POs		wt(TUNA) / BO68	
	Blend	Interesterified blend	Blend	Interesterified blend
C42	0.6	0.8	0.2	0.6
C44	0.2	1.1	0.5	1.0
C46	2.1	2.0	0.7	1.2
C48	19.3	6.2	2.1	2.3
C50	10.5	12.7	4.4	7.8
C52	7.9	12.3	13.4	11.9
C54	9.3	17.3	28.0	17.2
C56	12.2	15.7	12.8	18.4
C58	13.4	11.7	14.3	17.8
C60	12.9	11.8	12.3	10.9
C62	8.0	5.7	8.1	8.4
C64	3.5	2.7	3.2	2.5

Table 20

Evaluation results of example IX		
OIL	VISCOSITY cP	SAUTER MEAN PARTICLE DIAMETER μ M
Reference	5940	19.30
Sunflower oil / in(D40/BO68) 90/10	5580	16.01

Claims

- Triglyceride-composition, comprising at least two long chain poly-unsaturated fatty acids L_1 and L_2 , both having at least 3 unsaturations and having at least 20 carbon atoms from which L_1 is the most abundant and L_2 is the second most abundant, wherein the triglyceride composition contains at least 20 wt% of L_1 , while the weight ratio $L_1:L_2$ is at least 2, and the triglyceride composition also contains at least 15 wt%, of saturated fatty acids with 14 or more carbon atoms and wherein the weight ratio of saturated C_{18} : saturated C_{16} - C_{15} fatty acid residues is > 2 , whereas at least 5 wt%, preferably at least 10 wt%, most preferably at least 20 wt% of the saturated C_{14} + fatty acid residues is bonded on a triglyceride molecule, wherein at least L_1 and/or L_2 is present.
- Triglyceride composition according to claim 1, wherein the amount of L_1 is more than 30 wt%, while the weight ratio $L_1:L_2$ is at least 3.
- Triglyceride composition according to claims 1 or 2, wherein the amount of L_1 is at least 40 wt% and the weight ratio of $L_1:L_2$ is at least 3.5.
- Triglyceride composition according to claims 1 - 3, wherein the amount of saturated C_{14} + fatty acids is 15-50 wt%.
- Triglyceride composition according to claims 1 - 3, wherein the amount of C_{16} - C_{18} saturated fatty acids is more than 30 wt%, in particular more than 40 wt%.

6. Triglyceride composition according to claims 1 - 3, wherein the amount of C_{18} saturated fatty acid is more than 20 wt%, preferably more than 30 wt%.
7. Triglyceride composition according to claims 1 - 6, wherein $L_1 = \text{DHA}$ (= $C_{22:6}$).
8. Triglyceride composition according to claims 1 - 7, wherein $L_2 = \text{EPA}$ (= $C_{20:3}$).
9. Triglyceride composition according to claims 1 - 6, wherein $L_1 = \text{EPA}$ and $L_2 = \text{DHA}$.
10. Blends of triglycerides comprising:

0.3 - 95 wt%	of triglycerides according to claims 1 - 9, and
99.7 - 5 wt%	of a complementary fat, having a solid fat index at 10°C (N_{10}) that is either at least 5% more, or at least 5% less than the N_{10} of the triglycerides according to claims 1 - 9.
11. Blends of triglycerides, according to claim 10, comprising 5-80 wt%, in particular 20-70 wt% of the triglycerides according to claims 1 - 9, and 95 - 20 wt%, in particular 80-30 wt% of the complementary fat.
12. Blends according to claims 10 - 11, wherein the complementary fat has a solid fat content (NMR-pulse; not stabilized) of more than 15 at 20°C, preferably more than 20.
13. Blends according to claims 10 - 12, wherein the complementary fat is selected from cocoa butter equivalents, cocoa butter, palm oil or fractions thereof, palmkernel oil or fractions thereof, interesterified mixtures of above fats or fractions or hardened components thereof, or from liquid oils, such as sunflower oil, high oleic sunflower oil, soyabean oil, rapeseed oil, cottonseed oil, maize oil, safflower oil, high oleic safflower oil or MCT oils.
14. Blends according to claims 10 - 13, wherein the blend displays a solid fat content (NMR-pulse; not stabilized) of 0-85, preferably 10 - 70, most preferably 20 - 60 at 5°C and less than 30, preferably < 20, most preferably < 5 at 35°C.
15. Triglyceride compositions or blends containing them, according to claims 1 - 14, wherein the compositions or the blends contain an effective amount of an oxidation stabilizer, selected from the group consisting of: natural or synthetic tocopherols, BHT, BHA, free radical scavengers, enzymes with anti-oxidant properties.
16. Food products, comprising a fat phase, such as spreads, margarine, cream alternative, infant food, chocolate, confectionery, bakery products, sauces, ice-creams, ice-cream coatings, cheese, soups, mayonnaise, dressings, enteral or parental products, wherein the fat phase contains a fat according to claims 1 - 15.



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Application Number
EP 96 20 1020

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
Y	PATENT ABSTRACTS OF JAPAN vol. 17, no. 429 (C-1095), 10 August 1993 & JP-A-05 095792 (AGENCY OF IND SCIENCE & TECHNOL), 20 April 1993, * abstract *	1-16	A23D9/00 C11C3/00 A23L1/30
D,Y	--- BIOSCIENCE BIOTECHNOLOGY BIOCHEMISTRY, vol. 57, no. 12, 1993, TOKYO JP, pages 2202-2204, XP002010233 Y. ENDO ET AL.: "Retarded autoxidation of sardine oil with oleate" * the whole document *	1-16	
Y	--- EP-A-0 298 293 (FRESSENIUS AG) * page 3, line 31 - line 39 * * example 4 * * claims 1,11,20 *	1-16	
Y	--- JOURNAL OF THE AMERICAN OIL CHEMISTS' SOCIETY, vol. 71, no. 11, 1994, CHAMPAIGN US, pages 1277-1280, XP002010234 KUAN-HSIANG HUANG ET AL.: "Lipase-catalyzed incorporation of n-3 polyunsaturated fatty acids into vegetable oils" * the whole document *	1-16	TECHNICAL FIELDS SEARCHED (Int.Cl.6) A23D C11C A23L A61K C12P A23G A21D
D,A	--- EP-A-0 271 909 (GREEN CROSS CORPORATION) * column 3, line 4 - line 18 *	1	
D,A	--- EP-A-0 265 699 (THE NISSHIN OIL MILLS) * claims 1,4-7 *	1	
	--- -/-		
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 6 August 1996	Examiner Dekeirel, M
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, not published on, or after the filing date D : document cited in the application L : document cited for other reasons A : technological background O : non-written disclosure P : intermediate document	
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EP 0 739 591 A1 (2000.04.20)



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Application Number
EP 96 20 1020

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.4)
D,A	JOURNAL OF THE JAPAN OIL CHEMISTS' SOCIETY, vol. 42, no. 1, 1993, JP, pages 30-35, XP002010235 T. TOYOSHIMA ET AL.: "Preparation of polyunsaturated triacylglycerols via transesterification catalysed by immobilized lipase" * page 30, Abstract *	1	
A	EP-A-0 321 777 (THE JAPANESE RESEARCH AND DEVELOPMENT ASSOCIATION) * page 2, line 43 - page 3, line 9 *	1	
A	EP-A-0 609 001 (SCOTIA HOLDINGS PLC) * the whole document *	1-16	
D,A	US-A-5 151 291 (SHIGERU TOKAIRIN ET AL.) * column 2, line 48 - column 4, line 26 *	1-16	
A	JOURNAL OF FERMENTATION AND BIOENGINEERING, vol. 75, no. 4, 1993, pages 259-264, XP002010236 S. ADACHI ET AL.: "Acidolysis of sardine oil by lipase to concentrate eicosapentaenoic and docosahexaenoic acids in glycerides" * the whole document *	1	TECHNICAL FIELDS SEARCHED (Int.Cl.4)
A	WO-A-94 24889 (LODERS CROKLAAN) * page 3, line 23 - line 28 * * claims 1,4-10 *	1-16	
The present search report has been drawn up for all claims			
Place of search		Date of completion of the search	Examiner
THE HAGUE		6 August 1996	Dekeirel, M
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure F : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application I : document cited for other reasons A : number of the same patent family, corresponding document	

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Application Number
EP 96 20 1020

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	JOURNAL OF THE AMERICAN OIL CHEMISTS' SOCIETY, vol. 71, no. 3, 1994, CHAMPAIGN US, pages 331-334, XP002010237 YUKIHISA TANAKA ET AL.: "Synthesis of docosahexaenoic acid-rich triglyceride with immobilized Chromobacterium viscosum lipase" * the whole document *	1	
A	JOURNAL OF THE AMERICAN OIL CHEMISTS' SOCIETY, vol. 72, no. 2, 1995, CHAMPAIGN US, pages 239-243, XP002010238 S.B. PEDERSEN ET AL.: "Studies of the fatty acid specificity of the lipase from Rhizomucor miehei toward 20:1n-9, 20:5n-3, 22:1n-9 and 22:6n-3" * the whole document *	1	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 6 August 1996	Examiner Dekeirel, M
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EP 0 739 591 A1 (1996-08-06)